

# Adjacent MnOx clusters enhance the hydroformylation activity of rhodium single-atom catalysts

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## ABSTRACT

Hydroformylation reactions promoted by Rh single-atom catalysts typically exhibit a negative reaction order for CO and a positive reaction order for H<sub>2</sub> and alkenes. To enhance the catalytic activity, efforts have been concentrated on reducing the CO adsorption strength and/or enhancing the hydrogenation capacity at Rh sites. This report introduces an optimized Rh single-atom catalyst, utilizing positively charged Mn species to weaken the CO adsorption strength. Our strategy involves placing MnOx clusters in the proximity to the Rh single atom. This arrangement allows the reduction of Rh<sup>3+</sup> to produce electronically deficient Rh<sup>δ+</sup> species (1 < δ < 2), rather than the usual formation of the lower valence state Rh<sup>+</sup> species. The weakened CO adsorption strength on the more positively charged Rh<sup>δ+</sup> results in reduced CO coverage on the Rh active site, and enhanced adsorption of propylene. Our mechanistic study reveals that H<sub>2</sub> and CO adsorption on Rh catalyzes the reduction of adjacent Mn(IV) species, inducing the formation of a Rh-MnOx paired active site. The neighboring MnOx clusters hinder the extensive reduction of Rh<sup>3+</sup> to Rh<sup>+</sup>. This study presents MnOx as an inorganic ligand in Rh-MnOx pair site modifies the electronic properties of Rh sites to modulate the hydroformylation activity of Rh single-atom catalysts.

## 1. Introduction

The hydroformylation of olefins is one of the most significant industrial processes because the related product, aldehydes, are widely used as intermediates for synthesis of alcohols, esters, carboxylic acids and other fine chemicals [1,2]. Rh-based homogeneous catalysts are widely applied due to their outstanding activity and selectivity [3–5]. Compared with homogeneous catalysts, heterogeneous catalysts have lower activity and selectivity, but can be more easily recovered from the reaction mixture [1,2]. As the bridge between homogeneous and traditional heterogeneous catalysts, single atom catalysts (SAC) are expected to serve as catalysts for hydroformylation reactions with both high activity and selectivity [6,7].

Based on the mechanism of homogeneously catalysed

hydroformylation proposed by Heck and Breslow [8,9], the catalytic cycle involves: (I) activation of the catalyst by dissociation of one ligand, (II) the oxidative addition of olefin, (III) olefin insertion into the Rh-H bond, (IV) CO coordination, (V) CO insertion, (VI) oxidative addition of H<sub>2</sub>, (VII) reductive elimination of the resulting aldehyde with four transition states (TS) [4,10]. All these steps are possible to be the rate-limiting step (RLS), depending on the nature of the catalyst, reaction condition, and olefin etc. [4,10,11]. In homogeneous systems, most experimental and theoretical studies acknowledged that either olefin insertion into the Rh-H bond or reductive elimination of the resulting aldehyde, to be the RLS [12–14]. In many heterogeneous systems, CO insertion was the most energetically demanding step, for example, on Rh/MgO, Rh/CeO<sub>2</sub>, Rh/ReOx-Al<sub>2</sub>O<sub>3</sub>, Rh/WOx-Al<sub>2</sub>O<sub>3</sub>, Rh(111), and RhCo(111) surfaces [11,15–18]. The reaction order of CO in the olefin

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hydroformylation reaction is negative [16,19–22] due to the strong adsorption of CO on Rh. When CO insertion is the RLS, the key factor that improves reaction activity is to weaken CO adsorption strength to benefit its desorption and attack to hydrogenated olefine on SAC [10,11,15]. Efforts to regulate the CO adsorption strength on Rh active centers have been reported, often involving the integration of a secondary inactive component. For example, the introduction of RhP<sub>2</sub> [23], Rh-ReOx [16,24], and Rh-WOx [17] has been shown to draw electrons away from the Rh center. The key role of oxygen vacancy on support surface has been founded for reducible supports of CeO<sub>2</sub> [18] and SnO<sub>2</sub> [25] supported Rh SAC systems, which can modulate the direct coordination environment in single atom sites, via the exploitation of the oxide support's surface chemistry. Single-atom Rh/CeO<sub>2</sub> was also active for the hydroformylation of styrene coupled with water-gas shift reaction that benefitted the linear product formation [26]. Alternatively, the formation of intermetallic compounds such as RhZn [27] and RhCo [15] has also been employed. This approach leverages the separation (dilution) effects of the secondary inactive component to reduce the overly robust adsorption of CO.

Well-recognized for its varied and tunable valence states, in addition to practical advantages such as abundance and affordability, Mn has been deployed as a promoter to improve the activity of noble metal catalysts. Among currently reported systems, Rh catalysts promoted by MnOx are among the most effective for converting syngas into ethanol and other C<sub>2+</sub> oxygenates such as acetaldehyde and acetic acid [28–30]. The MnOx promoter functions as an electron-withdrawing ligand, partially oxidizing Rh atoms at the Rh-MnOx interface, which enhances the CO insertion in the desired reaction [28,30,31]. MnOx has also been demonstrated to control the electronic property of Pd in CO<sub>2</sub> hydrogenation reactions [32]. However, to the best of our knowledge, no systematic investigation has been conducted on the role of single-atom Rh-MnOx in hydroformylation reactions. As such, we seek to employ the electronic interaction between MnOx and Rh to diminish the CO adsorption strength on Rh, thereby enhancing the hydroformylation capability. To achieve highly dispersed and stable MnOx species, CeO<sub>2</sub> as the support has been selected due to its strong interaction with Mn [33–35].

In this study, we describe the synthesis, characterization, and comparative catalytic performance of the Rh-MnOx/CeO<sub>2</sub> catalyst versus the Rh/CeO<sub>2</sub> catalyst prepared by the static electronic adsorption (SEA) method. Encouragingly, the Rh-MnOx/CeO<sub>2</sub> catalyst indeed exhibited superior hydroformylation activity compared to the Rh/CeO<sub>2</sub> catalyst. We further studied the catalyst structural transformation and explored the mechanism underlying the enhanced activity. Specifically, X-ray photoelectron spectroscopy (XPS) and CO probe molecule Fourier Transform Infrared Spectroscopy during Temperature-Programmed Desorption (CO-FTIR-TPD) were used to determine the electronic structure and CO adsorption property, while *pseudo in-situ* XPS and *in-situ* FTIR spectroscopy were employed to identify the active species and its transformation under reaction condition.

## 2. Experimental and computational section

### 2.1. Catalyst preparation

y %MnOx/CeO<sub>2</sub> samples were prepared by incipient wetness impregnation method. In detail, the CeO<sub>2</sub> cube (synthesis method is described in SI) was immersed in appropriate amounts of aqueous solution of Mn (NO<sub>3</sub>)<sub>2</sub> • 4 H<sub>2</sub>O for 48 h then dried overnight at 80 °C and followed by calcination at 400 °C for 4 h. The obtained samples were labelled as y %MnOx/CeO<sub>2</sub>, where y represents the mass loading of Mn (y = 0.5, 1, 2.5 and 5).

Rh/y %MnOx-CeO<sub>2</sub> samples were prepared by SEA method. Typically, y %MnOx/CeO<sub>2</sub> support was impregnated by appropriate amounts of aqueous solution of [(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>RhCl<sub>3</sub>] under stirring, the solution pH was adjusted to 8 as determined by experiments in SI. Then,

the samples were obtained by washing with deionized water, centrifugal filtration, and drying at 80 °C for 12 h. Subsequently, the samples were calcined at 800 °C for 10 h. The resultant catalysts were labelled as Rh-y %MnOx/CeO<sub>2</sub>.

### 2.2. Catalytic activity test

The hydroformylation of propylene was performed in a 100 mL stainless-steel autoclave. After the addition of catalysts and 10 mL of n-heptane as solvent, the autoclave was pressurized with propylene (0.2 MPa), 1:1 molar ratio of CO and H<sub>2</sub> mixture (3 MPa). The reaction was performed at 100 °C with stirring at 300 rpm. After the completion of the reaction, the gas-phase components were collected and analyzed by gas chromatography (GC) using a Flame Ionization Detector (FID) detector. The liquid-phase components in the autoclave were collected by filtrating the reaction solution with a 0.45 μm polyethersulfone syringe filter and analysed by GC-FID using n-hexane as an internal standard. The filtrate was subjected to GC on a GC-2014-Shimadzu with a WondaCap FFAP capillary column and an FID. The recyclability of the catalyst was tested by centrifugal separation, and it was reused for the next run without washing. The kinetic study was conducted under the conversions <25 % by changing the catalyst mass. The reaction order of each reactant (CO, H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>) was studied by changing the pressure of one gas with the same total pressure by introducing Ar as balance gas.

### 2.3. Characterization

High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) analysis was carried out by a JEM-ARM200F microscope equipped with a spherical aberration collector at 200 kV. X-ray absorption spectroscopy (XAS) including extended X-ray absorption fine structure (EXAFS) and X-ray fine near-edge structure (XANES) at Rh K-edge were taken at the BL14B2 beamline at SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan) in fluorescence mode. IFEFFIT and Demeter packages were used as included in Athena and Artemis for the reduction of data (k range: 3–12). The X-ray edge energy was estimated using the first maximum of the first derivative of the absorption intensity. X-ray photoelectron spectroscopy (XPS) was conducted on a K-Alpha<sup>+</sup> spectrometer produced by Thermo Fisher Scientific. The X-ray source is Al K<sub>α</sub> (1486.6 eV) and the X-rays were monochromated. The calibration of the binding energy of Rh and Ce was based on that of C 1 s (284.8 eV) as the correction value. The sample was treated with CO, H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, CO+H<sub>2</sub>, or CO+H<sub>2</sub>+C<sub>3</sub>H<sub>6</sub> (1 bar) at 100 °C for 0.5 h in the fix bed reactor, after which it was transferred into the vacuum transfer stage in glove box for XPS measurement without exposure to air. *In-situ* FTIR spectroscopy was conducted by adsorption of CO and H<sub>2</sub> (molar ratio of CO: H<sub>2</sub> = 1:1) on catalyst until saturation, then purging off physically adsorbed species with the chemically adsorbed CO\* and H\* on Rh remained as active species. The reactivity of the adsorbed CO\* and H\* was investigated by introducing C<sub>3</sub>H<sub>6</sub> to the IR cell. The reaction of the pre-adsorbed CO\* and H\* with C<sub>3</sub>H<sub>6</sub> was carried out at 100 °C and a pressure of 1 atm. The *in-situ* FTIR spectra were collected under atmospheric pressure and gas phase, different from the catalytic evaluation condition.

## 3. Discussion

### 3.1. Establishment of Rh/MnOx-CeO<sub>2</sub> catalysts with different MnOx dispersion

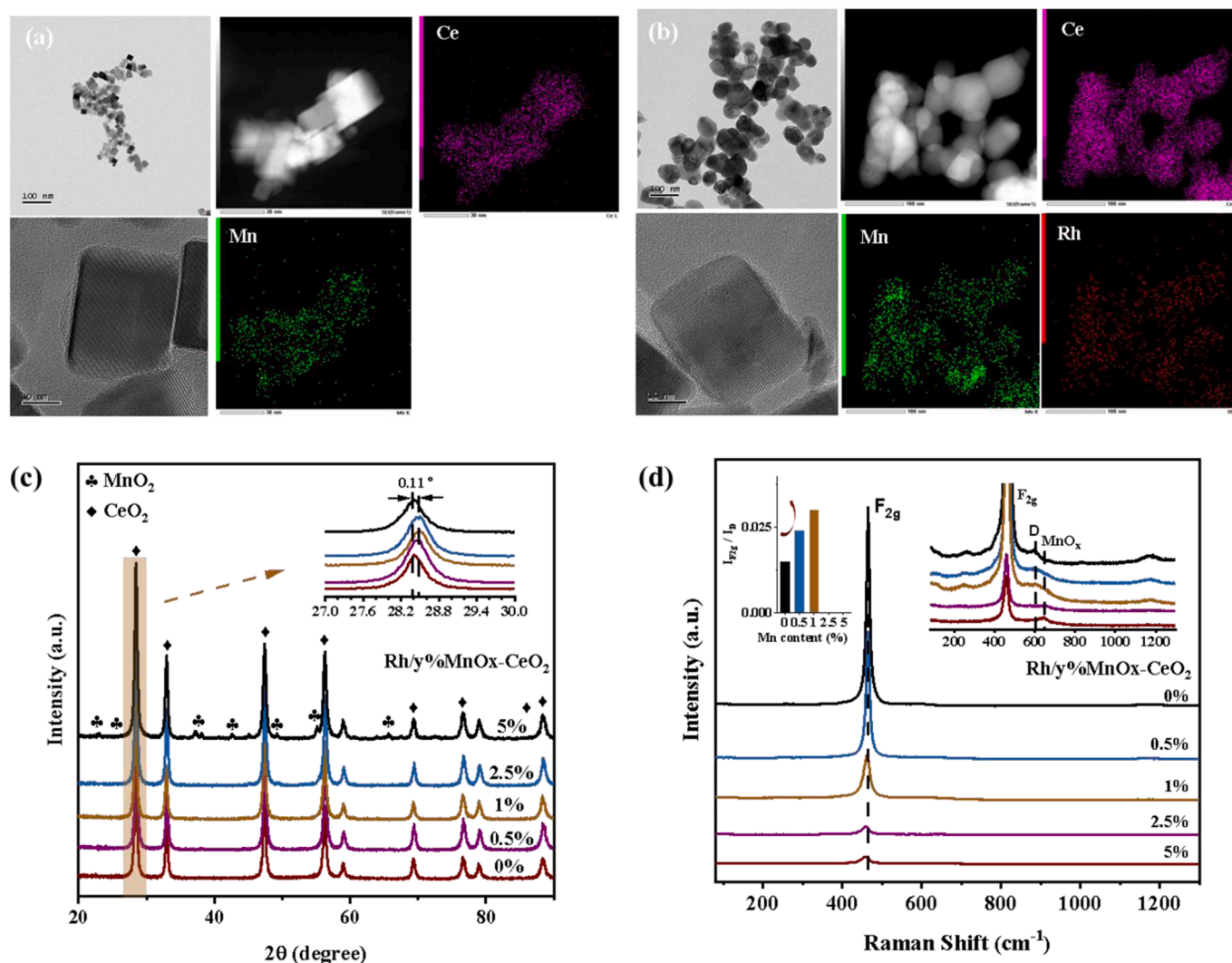
MnOx/CeO<sub>2</sub> was initially prepared via the impregnation method, followed by calcination at 400 °C. Subsequently, Rh was loaded using the SEA method and calcined at 800 °C (Figure S1-S3). At specific pH range, the ion (H<sup>+</sup> or OH<sup>-</sup>) that lies on the surface of MnOx and CeOx can be different because of the different PZC values of the metal oxides. Rh and MnOx islands are expected to be located near each other since the

pH of the  $[(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3\text{Rh}]^{3+}$  impregnation solution was adjusted to 8. This value is higher than the PZC of MnOx but lower than that of CeO<sub>2</sub>. At a pH of 8, MnOx surface carries a negative charge while the surface of CeO<sub>2</sub> is positively charged, resulting in the positively charged  $[(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3\text{Rh}]^{3+}$  being attracted to MnOx and repelled by CeO<sub>2</sub> (Scheme S1) [36,37]. Following this protocol, we established a series of Rh/MnOx-CeO<sub>2</sub> catalysts featuring a 0.06 % Rh loading amount and Mn loading amounts ranging from 0 % to 5 %. We also prepared MnOx/CeO<sub>2</sub> with Mn loading amounts varying between 0.5 % and 5 % as control samples. Inductively coupled Plasma-Optical Emission Spectrometer (ICP-OES)-determined actual loading amounts of Rh and Mn are listed in Table S1. After loading Mn and Rh, the Brunauer-Emmett-Teller (BET) surface area and pore size distribution of CeO<sub>2</sub> remained consistent (Figure S4 and Table S2).

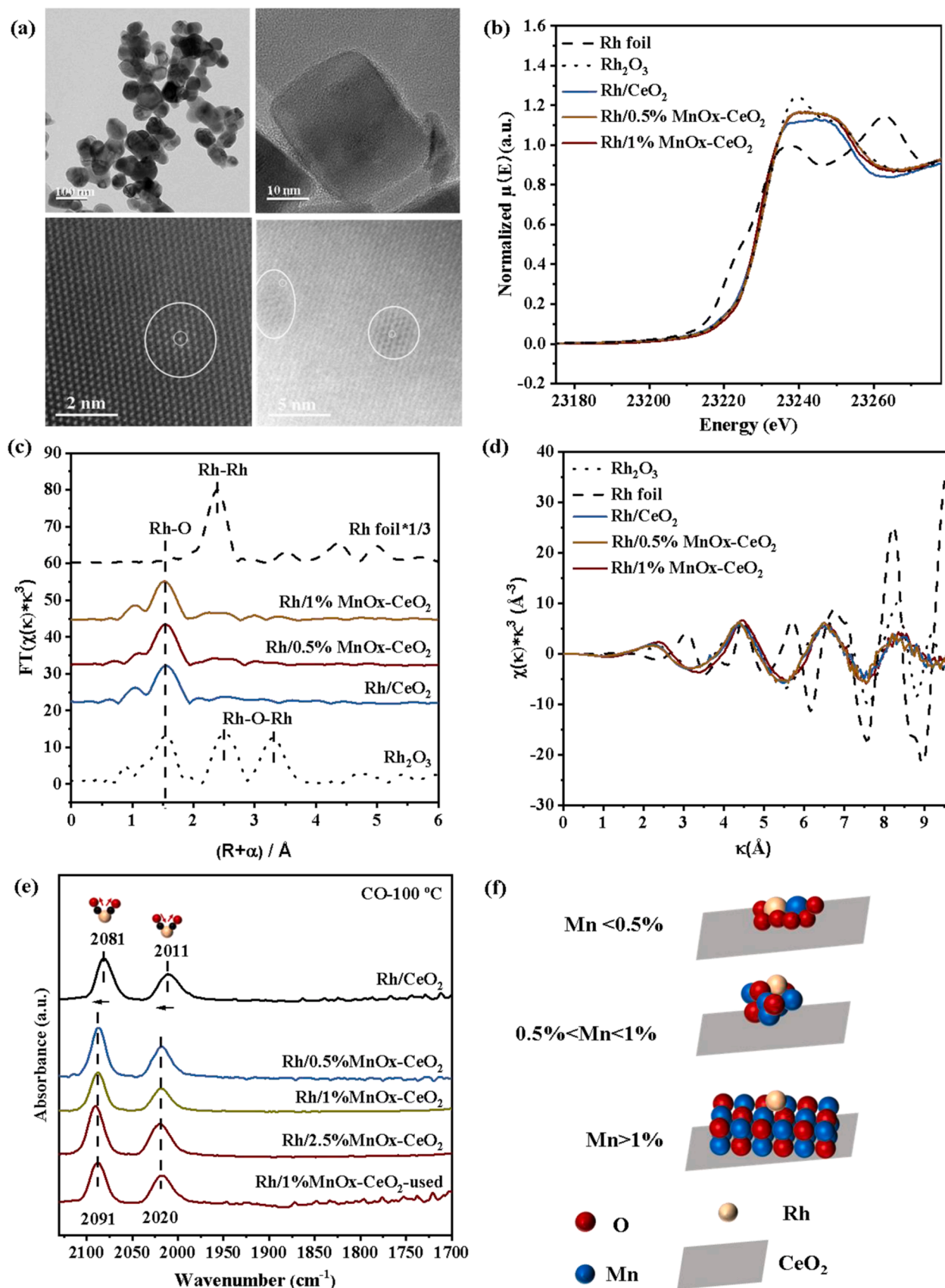
High-resolution transmission electron microscopy (HRTEM) images displayed in Fig. 1(a) and (b) confirm the successful preparation of CeO<sub>2</sub> nanocubes, with rounded edges observed after calcination at 800°C. EDS mapping reveals a high dispersion of Mn species on 1 %MnOx/CeO<sub>2</sub> and Rh/1 %MnOx-CeO<sub>2</sub> catalysts. Analysis of the X-Ray Diffraction (XRD) pattern (Fig. 1(c)) demonstrate an expansion of the CeO<sub>2</sub> crystal cell, as evidenced by a peak shift of 0.11°. Moreover, the Raman spectra (Fig. 1(d)) indicated an increased amount of oxygen vacancies, as reflected by the higher ratio value of  $I_{\text{D}}/I_{\text{F}_{2\text{g}}}$ . In detail, the signal at 465 cm<sup>-1</sup> corresponds to the F<sub>2g</sub> symmetry mode of the CeO<sub>2</sub> phase, while the weak

band at approximately 600 cm<sup>-1</sup> is associated with oxygen vacancies (D band) [38,39]. The intensity ratio of these two peaks ( $I_{\text{D}}/I_{\text{F}_{2\text{g}}}$ ) provides information about the concentration of the oxygen vacancies [40]. The enhanced concentration of oxygen vacancies was attributed to the strong interaction between Mn single atoms or MnOx clusters and CeO<sub>2</sub>, resulting in the incorporation of Mn cations into the CeO<sub>2</sub> lattice and the formation of oxygen vacancies to maintain the electronic properties of CeO<sub>2</sub> [41–45]. The XRD analysis of the 5 % Mn-doped catalyst reveals peaks attributed to bulky MnO<sub>2</sub>. Similarly, the Raman spectra detected a vibration signal near 641 cm<sup>-1</sup>, attributable to MnO<sub>2</sub> [46], in the 2.5 % and 5 % Mn-doped samples. Thus, when the Mn doping amount is below 1 %, the Mn species exhibit high dispersion on the surface of CeO<sub>2</sub>, leading to its incorporation into the CeO<sub>2</sub> lattice. A MnO<sub>2</sub> bulk phase is formed for the Mn doping amount > 1 %.

HAADF-STEM, EXAFS, and CO-FTIR results indicate atomically dispersed Rh located near MnOx (Fig. 2). Rh (the light dot) is positioned adjacent to the MnOx island rather than on CeO<sub>2</sub> as evident in HAADF-STEM images (Fig. 2(a)). It should be mentioned that the atomic number of Ce (58) is higher than that of Rh (45); the bright dots observed in the HAADF-STEM image are ascribed to the Rh single atoms only when viewed through the direction of the off-axis [47–49]. XANES profiles (Fig. 2(b)) suggest Rh is proximate to Rh<sup>3+</sup> state before reaction for both Rh/CeO<sub>2</sub> and Rh/MnOx-CeO<sub>2</sub> samples, because the edge energy and the white line intensity for all Rh samples closely resembled that of the



**Fig. 1.** HRTEM and mapping images of (a) 1 %MnOx/CeO<sub>2</sub> and (b) Rh/1 %MnOx-CeO<sub>2</sub> samples. (c) XRD patterns and (d) Raman spectra of Rh/y %MnOx-CeO<sub>2</sub>, where y % represent the mass percentage of Mn on CeO<sub>2</sub>.



**Fig. 2.** (a) TEM and HAADF-STEM images of Rh/1% MnOx-CeO<sub>2</sub>, (b) Rh K-edge XANES profiles, (c) Rh K-edge EXAFS spectra shown in R space, (d) Rh K-edge EXAFS shown in  $k^3$ -weighted  $k$ -space for Rh foil, Rh<sub>2</sub>O<sub>3</sub>, and Rh/y% MnOx-CeO<sub>2</sub>, (e) CO-FTIR spectra, and (f) proposed structure scheme of Rh/y% MnOx-CeO<sub>2</sub> with different Mn amounts (y %).



Rh<sub>2</sub>O<sub>3</sub> reference. A blue shift (2081 and 2011 cm<sup>-1</sup> to 2091 and 2020 cm<sup>-1</sup>) of bands attributed to Rh(CO)<sub>2</sub> species in the CO probe molecule-FTIR spectra (Fig. 2(e)) reveals the electronic interaction between Rh and adjacent MnOx. The Rh K-edge EXAFS profiles in Fig. 2(c) and fitting curves in Figure S5 unveil a first shell at approximately 1.5 Å corresponding to Rh-O, with no presence of Rh-Rh shell at roughly 2.5 Å, suggesting atomically dispersed Rh species for all the Rh/CeO<sub>2</sub> and Rh/y %MnOx-CeO<sub>2</sub> catalysts. The Rh K-edge EXAFS spectra in Fig. 2(d) demonstrate that Rh/y %MnOx-CeO<sub>2</sub> and Rh/CeO<sub>2</sub> profiles more closely resemble Rh<sub>2</sub>O<sub>3</sub> than Rh foil. The CO probe molecule FTIR spectroscopy analysis in Fig. 2(e) displays typical symmetric and asymmetric stretching vibration modes (around 2091 and 2020 cm<sup>-1</sup>) of the positively charged Rh(CO)<sub>2</sub> species for all the Rh/y %MnOx-CeO<sub>2</sub> catalysts. The absence of a band (1700–1800 cm<sup>-1</sup>) attributed to CO bridge adsorption on Rh cluster/nanoparticle, further confirms the atomic dispersion of Rh. From these characterizations, we depict a catalyst structure with varying dispersion of Mn species in Fig. 2(f). When the Mn loading amount is less than 0.5 %, Rh and Mn are atomically dispersed; at a Mn amount of 1 %, Rh is located on MnOx cluster; further increasing the Mn amount to more than 1 % leads to a MnO<sub>2</sub> nanoparticle supported single-atom Rh structure.

### 3.2. Catalytic reactivity for propylene hydroformylation

In a syngas atmosphere, propylene can be hydrogenated to propane or undergo hydroformylation to butyraldehyde. During hydroformylation, CO is inserted into the terminal and internal positions of the C=C bond in propylene, yielding linear and branched butyraldehyde, respectively. The catalytic performance of Rh/CeO<sub>2</sub> and Rh/y %MnOx-CeO<sub>2</sub> was evaluated in propylene hydroformylation under 3 MPa syngas and 100 °C. Before measurements, it has been confirmed that no thermodynamic equilibrium or mass transfer limitations exist in the system (Figure S6). As shown in Fig. 3(a), only butyraldehyde was formed as the product, demonstrating 100 % chemo-selectivity. The Turnover Frequency (TOF) exhibits a volcano-shaped curve with increasing Mn amounts for hydroformylation, achieving the highest value (~7200 h<sup>-1</sup>) at Mn amount = 1 %. The ratio of linear to branched butyraldehyde (l/b), an indicator of regio-selectivity, remains constant at ~0.67 as the Mn amount increases, suggesting that Mn addition does not impact the regio-selectivity for Rh. Although the catalyst system has no steric hindrance effect, the l/b ratio is not 1 but 0.67, indicating that the catalyst structure and reaction condition in this work prefer the formation of iso-butanal. Fig. 3(b) shows that Rh/1 %MnOx-CeO<sub>2</sub> exhibits the lowest apparent activation barrier (E<sub>a</sub>) for butyraldehyde formation, possibly because the Mn doping aids the formation of more active Rh species for propylene hydroformylation.

The recyclability of Rh/1 %MnOx-CeO<sub>2</sub> was evaluated by conducting successive rounds of reaction (Fig. 3(c)). Remarkably, 90 % of the original activity was retained after five cycles. According to the CO-FTIR result (Fig. 2(e)), the Rh species post-reaction remained atomically dispersed. Negligible activity (<5 %) was detected in the supernatant obtained by filtering the catalysts from the reaction solution, reinforcing that the catalytic activity primarily stems from the Rh supported on CeO<sub>2</sub>, not from the leached Rh species.

The power law equation for propylene hydroformylation can be expressed as

$$r = k P_{\text{CO}}^{\alpha} P_{\text{H}_2}^{\beta} P_{\text{C}_3\text{H}_6}^{\gamma}$$

in which  $k$  and  $P_{\text{CO}}$ ,  $P_{\text{H}_2}$ ,  $P_{\text{C}_3\text{H}_6}$  stand for the reaction rate constant and the partial pressure of CO, H<sub>2</sub>, and C<sub>3</sub>H<sub>6</sub>, respectively; while  $\alpha$ ,  $\beta$  and  $\gamma$  are the reaction order for CO, H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>, respectively. As illustrated in Fig. 3(d-f), the values calculated for CO ( $\alpha$ ), H<sub>2</sub> ( $\beta$ ), and C<sub>3</sub>H<sub>6</sub> ( $\gamma$ ) at 100 °C for Rh/1 %MnOx-CeO<sub>2</sub> are -0.44, 0.36, and 0.52, respectively. Compared with Rh/CeO<sub>2</sub> ( $\alpha$  = -1.2), the reactor order of CO has moved towards a less negative value. This implies that CO is more weakly

adsorbed on Rh, a finding further confirmed by the CO-FTIR-TPD and CO-TPD results showing a reduction in the strength of CO adsorption over Rh/1 %MnOx-CeO<sub>2</sub>. The weakened CO adsorption is beneficial for C<sub>3</sub>H<sub>6</sub> adsorption, as evidenced by the reduced C<sub>3</sub>H<sub>6</sub> order ( $\gamma$ ) value from 0.94 on Rh/CeO<sub>2</sub> to 0.52 on the Rh/1 %MnOx-CeO<sub>2</sub> catalyst.

The H<sub>2</sub> order ( $\beta$ ) for Rh/1 %MnOx-CeO<sub>2</sub> ( $\beta$  = 0.36) is similar to that of Rh/CeO<sub>2</sub> ( $\beta$  = 0.42), signifying that 1 % MnOx doping doesn't impede H<sub>2</sub> activation. In contrast, the H<sub>2</sub> reaction order for the catalyst doped with 2.5 % Mn significantly escalates to 0.94, suggesting a hampered H<sub>2</sub> activation ability. H<sub>2</sub>-TPR and H<sub>2</sub>-TPD results reveal a high reduction temperature (starting from 150 °C) for RhOx on the 2.5 % Mn-doped catalyst, suggesting increased barrier for Rh<sup>3+</sup> reduction due to the diminished H<sub>2</sub> adsorption strength.

For these experiments, the Rh/y %MnOx-CeO<sub>2</sub> ( $y < 1$  %) catalysts bearing Rh-MnOx clusters exhibit enhanced CO reaction order and reduced C<sub>3</sub>H<sub>6</sub> reaction order. This pattern, coupled with a lower activation energy, suggests that the Rh-MnOx cluster active species can mitigate the vigorous adsorption of CO on Rh and facilitates the adsorption of C<sub>3</sub>H<sub>6</sub>, thereby enhancing the overall activity.

### 3.3. The modification of CO adsorption property on Rh by adjacent MnOx species

We conducted a series of TPR and TPD experiments to explore the metal-support interactions and CO adsorption property in different catalysts. The H<sub>2</sub>-TPR profile of pure CeO<sub>2</sub> (Fig. 4(a)) features two peaks, attributable to the reduction of surface CeO<sub>2</sub> (around 380 °C) and bulk CeO<sub>2</sub> (approximately 720 °C). For Rh/CeO<sub>2</sub> and Rh/MnO<sub>2</sub>-CeO<sub>2</sub>, the hydrogen consumption for the peak at 50–200 °C was estimated to be 2–4.5 mmol/g, much higher than the theoretical amount (8.7 μmol/g) needed for Rh<sup>3+</sup> reduction (Figure S4). The remaining hydrogen was plausibly used for surface reduction of MnOx and CeO<sub>2</sub>. The introduction of Rh stimulates the co-reduction of RhOx and surface CeO<sub>2</sub> (around 90 °C). Likewise, Rh/y %MnOx-CeO<sub>2</sub> allows for the co-reduction of MnOx, RhOx, and surface CeO<sub>2</sub>. Due to the atomic dispersion of Rh, there is only Rh-O-Ce structure around Rh for Rh/CeO<sub>2</sub> catalysts, which is reduced at 88 °C as indicated by the first signal in Fig. 4(a). Likewise, only Rh-O-Mn structure around Rh center is existed for Rh/MnO<sub>2</sub> catalyst, which showed a much higher reduction temperature (246 °C) (Figure S7). Thus, as the Mn content increased to 2.5 %, more Rh-O-Mn structure is formed, shifting the peak temperature from 88 °C to 230 °C (Fig. 4(a)). This observation aligns with XPS results demonstrating a gradual decrease in Rh's electronic density with increasing MnOx loading amount for Rh/y %MnOx-CeO<sub>2</sub> (Fig. 4(b)), which may stem from the strong interaction between Rh and MnOx-CeO<sub>2</sub>. In line with this, the band doublet attributed to the symmetric and asymmetric stretching of Rh(CO)<sub>2</sub> species on Mn-doped catalysts (~2086 and ~2015 cm<sup>-1</sup>) showed a blue shift compared with that on Rh/CeO<sub>2</sub> (2079 and 2008 cm<sup>-1</sup>), hinting at a lower electronic density of single-atom Rh for Rh/MnOx-CeO<sub>2</sub> (Fig. 4(c,d,e,f)). Moreover, the generated Rh<sup>δ+</sup> species exhibit diminished CO adsorption strength due to the reduction of available electrons for CO coordination (Fig. 4(c,d,e,f)).

The CO-FTIR-TPD spectra (Fig. 4(c)) reveal two signals at 2079 cm<sup>-1</sup> and 2008 cm<sup>-1</sup>, linked to the symmetric and asymmetric vibration of single atom Rh(CO)<sub>2</sub> species on Rh/CeO<sub>2</sub>. A 2092 cm<sup>-1</sup> band is related to single-atom Rh(CO) species, which also has been observed in Rh/γ-Al<sub>2</sub>O<sub>3</sub> [50] and Rh/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> [51] systems, consequent to the desorption of one CO from Rh(CO)<sub>2</sub> species. Rh(CO)<sub>2</sub> species desorb gradually with temperature increase, persisting at 200 °C for Rh/CeO<sub>2</sub>. For Mn-doped samples at 0.5 %, 1 %, and 2.5 % (Fig. 4(d), (e), and (f)), the CO adsorption strength on single-atom Rh weakens as evidenced by a lower full desorption temperature below 180 °C, compared to over 200 °C on Rh/CeO<sub>2</sub>. As shown in Fig. 4(g) and (h), the CO desorption rate on Rh/CeO<sub>2</sub> is significantly lower than on the Mn-doped samples, further suggesting that Mn doping weakens the CO adsorption strength. Specifically, the CO desorption rate on Rh/CeO<sub>2</sub> is roughly 1/3 of that on

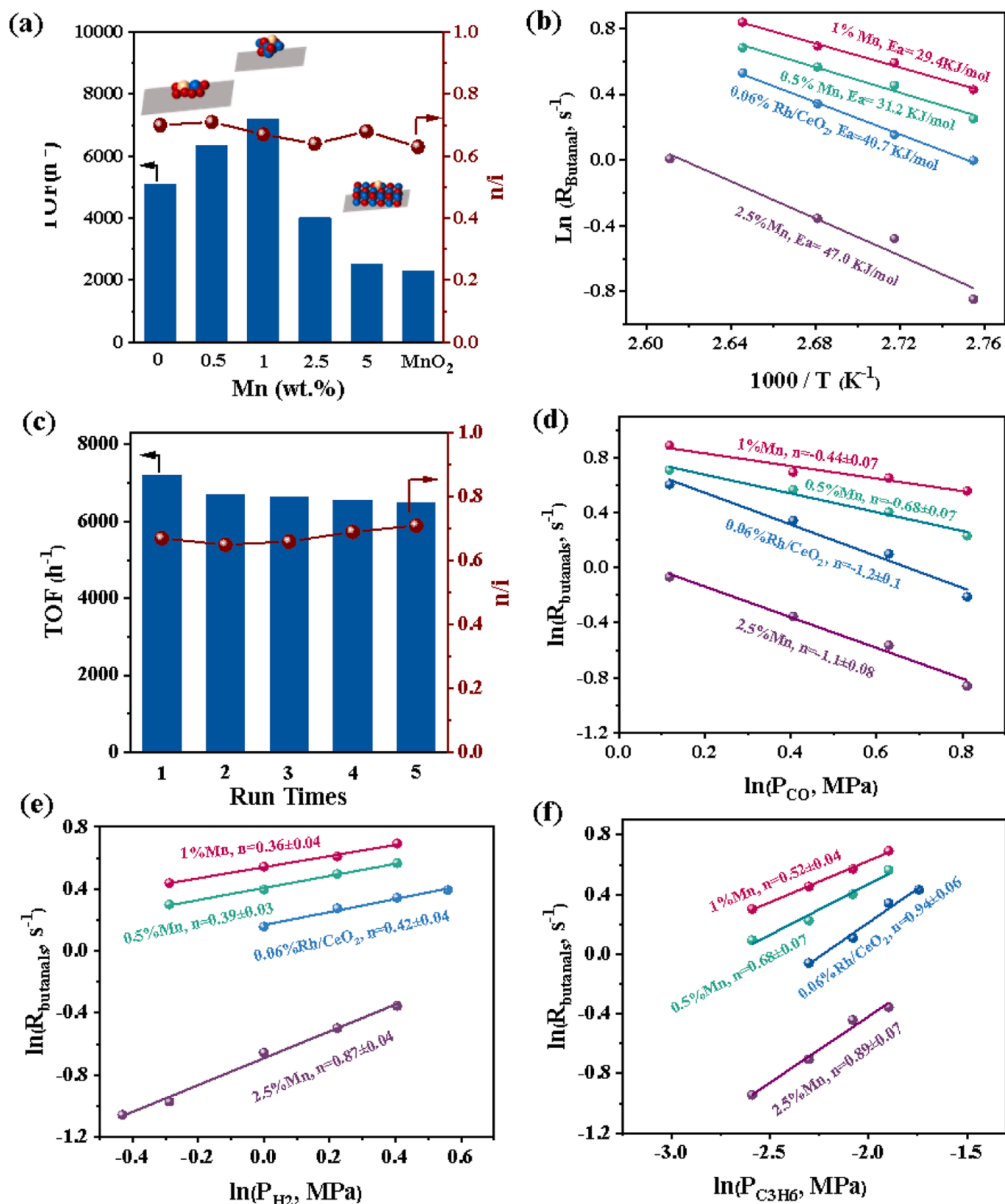
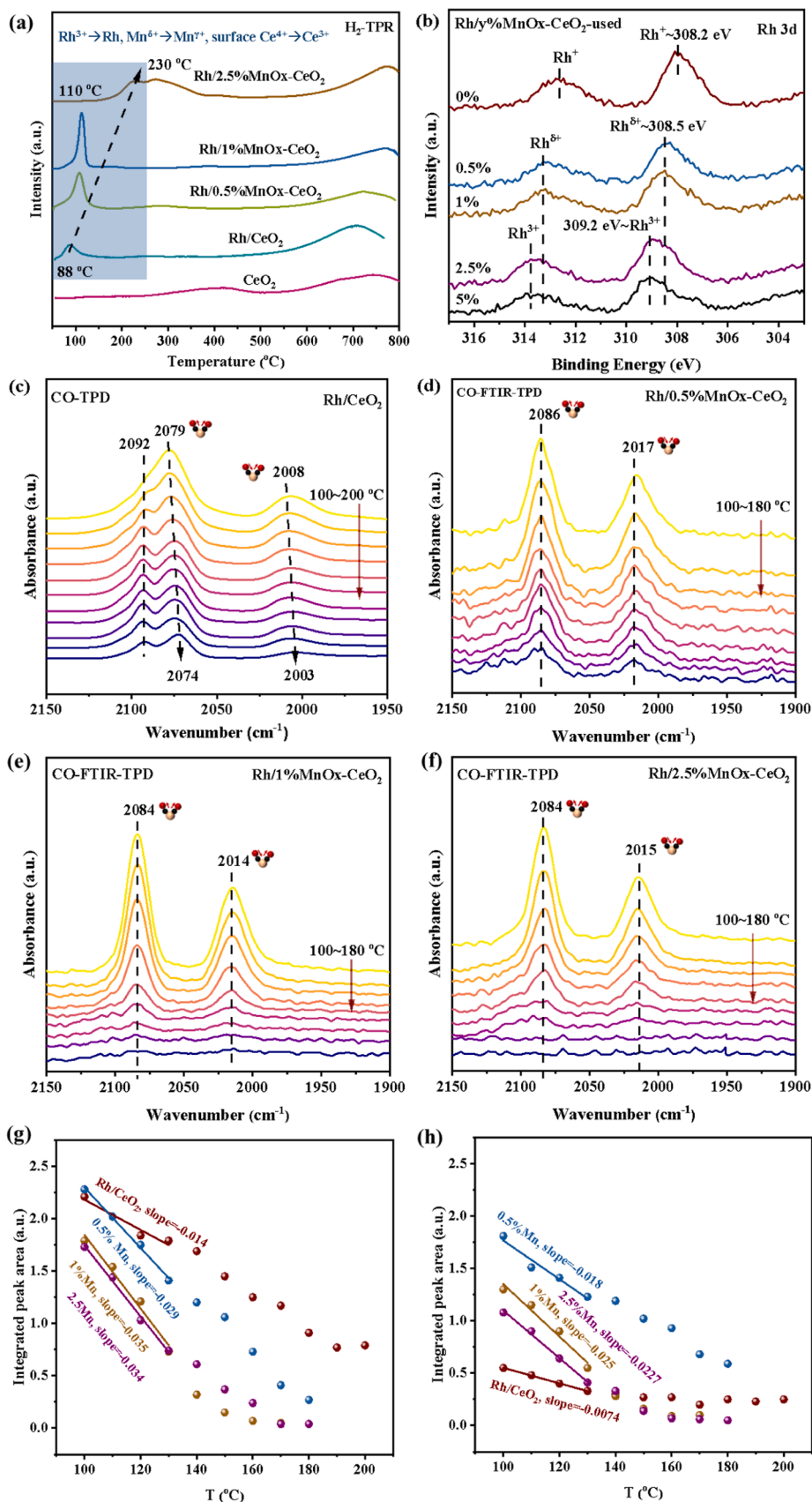


Fig. 3. (a) The effect of Mn amount on TOF and selectivity for 0.06 % Rh/CeO<sub>2</sub>-cube. (b) Arrhenius plots of 0.06 % Rh/y %MnO<sub>x</sub>-CeO<sub>2</sub> with different amount of Mn. (c) Recycling performance of 0.06 % Rh/1 %MnO<sub>x</sub>-CeO<sub>2</sub> for the hydroformylation of propylene. The propylene conversion is between 20 % and 25 %. (d) CO, (e) H<sub>2</sub>, and (f) C<sub>3</sub>H<sub>6</sub> reaction order of Rh/y %MnO<sub>x</sub>-CeO<sub>2</sub> catalysts at 100 °C. Reaction condition: 100 °C, 3 MPa CO/H<sub>2</sub> (1:1), 0.2 MPa propylene, 20 mg catalyst, 0.5 h, 300 rpm. Kinetic experiments were examined under the conversions <25 % by varying the catalyst amount. For determining the reactant orders, make sure P<sub>Total</sub> = 3.2 MPa, catalyst mass = 0.1 g, (d) P<sub>C<sub>3</sub>H<sub>6</sub></sub> = 0.2 MPa, P<sub>H<sub>2</sub></sub> = 1.5 MPa, balance gas: He, (e) P<sub>C<sub>3</sub>H<sub>6</sub></sub> = 0.2 MPa, P<sub>CO</sub> = 1.5 MPa, balance He, (f) P<sub>CO</sub> = P<sub>H<sub>2</sub></sub> = 1.5 MPa, balance He.



**Fig. 4.** (a) H<sub>2</sub>-TPR for Rh/y%MnOx-CeO<sub>2</sub> with different amounts of Mn, (b) Rh 3d XPS spectra for Rh/y%MnOx-CeO<sub>2</sub> with different amount of Mn after reaction. CO-FTIR-TPD spectra for (c) Rh/CeO<sub>2</sub>, (d) Rh/0.5%MnOx-CeO<sub>2</sub>, (e) Rh/1%MnOx-CeO<sub>2</sub>, and (f) Rh/2.5%MnOx-CeO<sub>2</sub>. During CO-FTIR-TPD, CO is adsorbed at 100 °C for 30 min, and the programmed temperature increase rate is 5 °C/min. The evolution of integrated peak area at (g) 2074–2086 cm<sup>-1</sup> and (h) 2008–2017 cm<sup>-1</sup> with increasing temperature for Rh/CeO<sub>2</sub>, and Rh/x%MnOx-CeO<sub>2</sub>.

the 1 % Mn-doped catalyst. The Rh(CO) species is existed on Rh/CeO<sub>2</sub> sample, but not on Rh/MnOx-CeO<sub>2</sub> sample, due to the weakened CO adsorption strength on Rh after MnOx doping. Hence, relative to Rh<sup>+</sup> on Rh/CeO<sub>2</sub>, Mn doping inhibits the reduction of RhOx to Rh<sup>+</sup>, resulting in Rh<sup>δ+</sup> species with weaker CO adsorption capacity. Adsorption properties for propylene, H<sub>2</sub>, and butanal are discussed in SI (Figure S7–10), and the results show increased adsorption sites for C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub> and butanal due to the decreased CO adsorption coverage.

### 3.4. The formation mechanism of Rh-MnOx active species and its role in enhancing hydroformylation activity

We implemented a sequence of spectroscopic analyses under varying reactant conditions to understand the formation mechanism of Rh-MnOx active species. The CO-FTIR results (Fig. 5(a)) exhibit a blue shift (around 10 cm<sup>-1</sup>) for bands linked to Rh(CO)<sub>2</sub> after incorporating 0.5 % and 1 % Mn to Rh/CeO<sub>2</sub>, which aligns with Rh's higher valance state in these catalysts as shown by the XPS analysis (Fig. 4(b)). In the CO-FTIR analysis, OCO\*, HCOO\*, and CO<sub>2</sub> species were observed on Rh/MnOx-CeO<sub>2</sub> and MnOx-CeO<sub>2</sub> during the co-feeding of CO and H<sub>2</sub> (Fig. 5(c)). The OCO\* species gradually strengthen over the HCOO\* species, and more CO<sub>2</sub> is generated as the Mn content increases for Rh/MnOx-CeO<sub>2</sub>. This suggests that neighbouring MnOx species facilitate the conversion of CO to CO<sub>2</sub>, originating from the reduction of Rh and Mn oxide, which matches the formation of CO<sub>2</sub> seen in the CO-TPD results (Figure S11). As shown in the FTIR spectra for MnOx-CeO<sub>2</sub> after treated by reactants (Figure S12), the broad signal within 1950–2150 cm<sup>-1</sup> observed on MnOx-CeO<sub>2</sub> samples can be related to CO adsorbed on reduced MnOx cluster surface (denoted as Mn(CO)<sub>x</sub>) [29,52,53]. Introducing Rh to MnOx-CeO<sub>2</sub> results in an additional wide band in 1600–1800 cm<sup>-1</sup> on 0.5 % and 1 % Mn doped samples (Fig. 5(b)), which is too low to be caused by a CO bridge bonded to several Rh atoms by carbon atoms alone (normally > 1800 cm<sup>-1</sup>). Lisitsyn et al. [54] identified comparable frequencies at 1725 cm<sup>-1</sup> and 1696 cm<sup>-1</sup>, which have been hypothesized to be CO on metal/oxide interfacial sites, with C and O being bound to Rh<sup>δ+</sup> and Mn<sup>7+</sup> cations, respectively [55,56]. Based on this, we tend to assign our signal to be related to Rh-C-O-Mn species. The strong IR intensity suggests that a substantial amount of the surface Rh atoms are in close vicinity to Mn cations [57]. The Rh-C-O-Mn entities promote the CO desorption into CO<sub>2</sub>, forming Rh(CO) active species. In short, during the process CO adsorbed on Rh reduces the Mn=O bond, aids in CO desorption from Rh(CO)<sub>2</sub>, forming the initial Rh(CO) active species. The CO-FTIR results under different reactant treatment (Figure S13) suggest that C<sub>3</sub>H<sub>6</sub> adsorption enhances the reduction of MnOx into Mn(CO)<sub>x</sub> species by CO. This may be due to the steric hindrance effect, whereby the absorption of C<sub>3</sub>H<sub>6</sub> causes the migration of CO on Rh to the adjacent Mn=O site, leading to the reduction of MnOx and the formation of Mn(CO)<sub>x</sub> species.

For the valance state evolution of active species, after introducing CO, the Rh<sup>3+</sup> (309.2 eV) and Mn<sup>4+</sup> (642.7 eV) species is reduced to Rh<sup>7+</sup> (2<γ<3) (308.8 eV) and Mn<sup>3+</sup> (641.4 eV), which is further reduced to Rh<sup>δ+</sup> (308.5 eV) and Mn<sup>2+</sup> (640.4 eV), respectively, after introducing H<sub>2</sub> or/and C<sub>3</sub>H<sub>6</sub> under reaction conditions (Fig. 5(d) and (e)). Thus, we deduce that CO can reduce Rh<sup>3+</sup> to Rh<sup>7+</sup>, and Mn<sup>4+</sup> to Mn<sup>3+</sup> with CO<sub>2</sub> production. On introducing additional H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>, Rh<sup>7+</sup> and Mn<sup>3+</sup> can be further reduced to Rh<sup>δ+</sup> and Mn<sup>2+</sup>, respectively. Figure S14 further suggested that oxygen vacancy and Ce<sup>3+</sup> are also increased under reaction condition. Based on these, the mechanism for active species formation is proposed in Fig. 5(f), in which highly dispersed Rh-MnOx species are transformed to (CO)Rh<sup>δ+</sup>-Mn<sup>2+</sup>(CO)<sub>x</sub> as pair active species under the reaction condition. The proposed active center structures are shown in Fig. 5(g). In contrast, on 2.5 % and 5 % Mn samples, MnOx nanoparticle is hard to be reduced to form Mn<sup>2+</sup> (Figure S14–18).

We further investigated the reaction mechanism by performing an in-situ FTIR spectroscopy analysis. The catalyst was initially pretreated with CO and H<sub>2</sub>, followed by purging with C<sub>3</sub>H<sub>6</sub> while concurrently

recording the FTIR signal. The results (Fig. 6(a) and (c)) revealed that the band of Rh(CO) (2106 cm<sup>-1</sup>), emerging from CO desorption from Rh(CO)<sub>2</sub>, increased before decreasing, which is accompanied with the formation of butyraldehyde (1700 cm<sup>-1</sup>), indicating Rh(CO) is the active species to attack C<sub>3</sub>H<sub>6</sub> to form butyraldehyde. The rate of Rh(CO)<sub>2</sub> consumption to produce active Rh(CO) species is greater on Rh/1 % MnOx-CeO<sub>2</sub> than on Rh/CeO<sub>2</sub>. This is evidenced by the persistence of peaks associated with Rh(CO)<sub>2</sub> (2070 and 1992 cm<sup>-1</sup>) on Rh/CeO<sub>2</sub> even after an 8-minute reaction period, as shown in Fig. 6(b). On the contrary, these peaks (2077 and 2009 cm<sup>-1</sup>) almost vanish after just 7 minutes of reaction on Rh/1 %MnOx-CeO<sub>2</sub>, as depicted in Fig. 6(d). Moreover, the consumption rate of formed Rh(CO) active species is also faster on Rh/1 %MnOx-CeO<sub>2</sub> than on Rh/CeO<sub>2</sub>. This is evidenced by the complete consumption of Rh(CO) on the former catalyst within 4 minutes, while the same species continues to exist on the latter catalyst even after an 8-minute reaction. In short, the formation and consumption of Rh(CO), in conjunction with butanal, happened in a higher rate on Rh/1 %MnOx-CeO<sub>2</sub> than on Rh/CeO<sub>2</sub>. The improved hydroformylation activity of Rh/1 %MnOx-CeO<sub>2</sub> compared to Rh/CeO<sub>2</sub> is driven by an enhanced turnover rate of the key Rh(CO) active species. This enhancement is attributed to the adjacent MnOx weakening the CO adsorption strength on Rh<sup>δ+</sup>, facilitating CO desorption from Rh(CO)<sub>2</sub> and subsequent formation of Rh(CO) active species. This process also aids the consumption of the formed Rh(CO) active species, where CO desorbs and reacts with activated propylene, leading to butanal formation.

The in-situ FTIR results for Rh/0.5 %MnOx-CeO<sub>2</sub> showed that the turnover of active Rh(CO) species is slower than on Rh/1 %MnOx-CeO<sub>2</sub>, for Rh/2.5 %MnOx-CeO<sub>2</sub> which showed no formation of Rh-MnOx species and much lower activity (Figure S19). We also record the FTIR spectra for catalysts after reaction under Ar purging and find the regeneration of Rh(CO)<sub>2</sub> species after reaction on Rh-MnOx catalysts (Figure S20 and S21). Based on these findings, we proposed the hydroformylation reaction mechanism on Rh-MnOx as shown in Scheme S2.

## 4. Conclusion

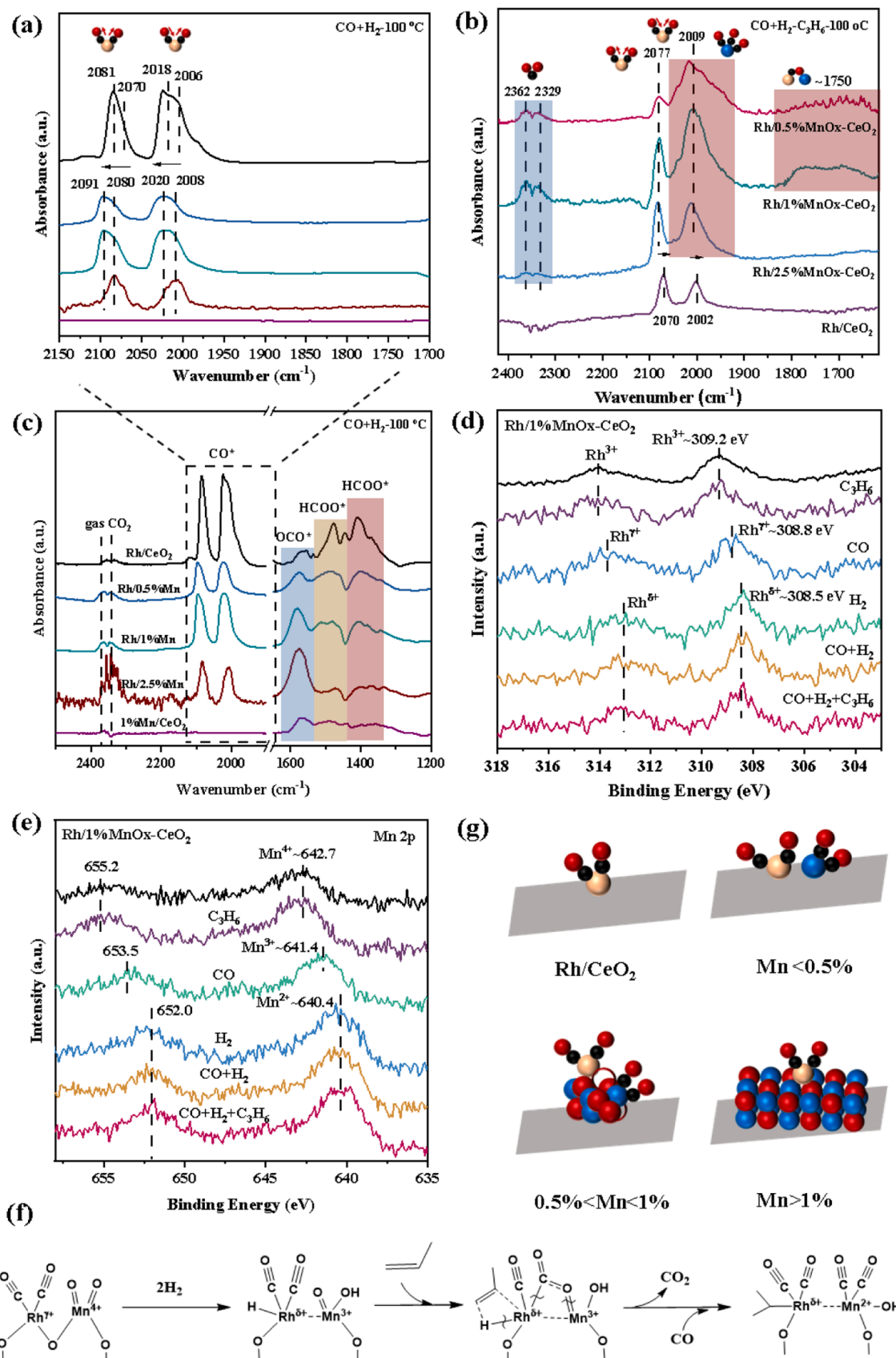
In conclusion, a combination of EXAFS, CO-FTIR, and HAADF-STEM characterizations confirm that on SEA method prepared Rh/γ %MnOx-CeO<sub>2</sub> catalysts, Rh is atomically dispersed on the CeO<sub>2</sub> support with neighboring MnOx clusters when Mn loading is less than 1 %. These well-dispersed MnOx clusters are easily reduced to Mn<sup>2+</sup> under reaction conditions, forming Rh-MnOx pair sites that enable the generation of electronically deficient Rh species. The resultant Rh<sup>δ+</sup> (1 < δ < 2) cations, characterized by weakened CO adsorption strength, ease the desorption of CO from Rh, facilitating the activation of propane during the rate-determining step. Our *pseudo* in-situ XPS and in-situ FTIR findings suggest H<sub>2</sub>, CO and C<sub>3</sub>H<sub>6</sub> co-adsorption on Rh assist in reducing the Mn=O bond to create Rh-MnOx pair active sites, which only happen in the case of highly dispersed MnOx, not MnO<sub>2</sub> nanoparticles.

This study establishes Rh-MnOx pair active sites on the CeO<sub>2</sub> surface, demonstrating enhanced activity compared to the Rh single atom catalyst for propylene hydroformylation. The findings offer insights for the modification of single atom active sites using inorganic cluster as electronic ligands to improve hydroformylation activity.

## CRedit authorship contribution statement

**Ying Zheng:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Qi Yang:** Methodology, Formal analysis. **Sikai Wang:** Formal analysis. **Shinya Furukawad:** Resources, Formal analysis. **Maoshuai Li:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Ning Yan:** Resources, Writing – review & editing, Supervision. **Xinbin Ma:** Conceptualization, Resources, Writing – review & editing, Supervision, Project





**Fig. 5.** (a) Magnified picture of (c) in range of 1700–2150  $\text{cm}^{-1}$ . (c) FTIR spectra for different catalysts after treatment by  $\text{CO}$  and  $\text{H}_2$  at 100  $^{\circ}\text{C}$ . (b) The FTIR results of different  $\text{Rh}/y\% \text{MnO}_x\text{-CeO}_2$  catalysts after in-situ reaction co-feeding with  $\text{CO}$ ,  $\text{H}_2$  and  $\text{C}_3\text{H}_6$ . (d) Rh 3d XPS results after different gas atmosphere treating for  $\text{Rh}/1\% \text{MnO}_x\text{-CeO}_2$  catalyst. (e) Mn 2p XPS spectra after different gas atmosphere treating for  $\text{Rh}/1\% \text{MnO}_x\text{-CeO}_2$  catalyst. (f) Proposed possible formation process of initial Rh-Mn dual metal active sites. (g) Proposed Rh-MnOx active species structure on  $\text{Rh}/y\% \text{MnO}_x\text{-CeO}_2$  catalyst surface with different loading of Mn.

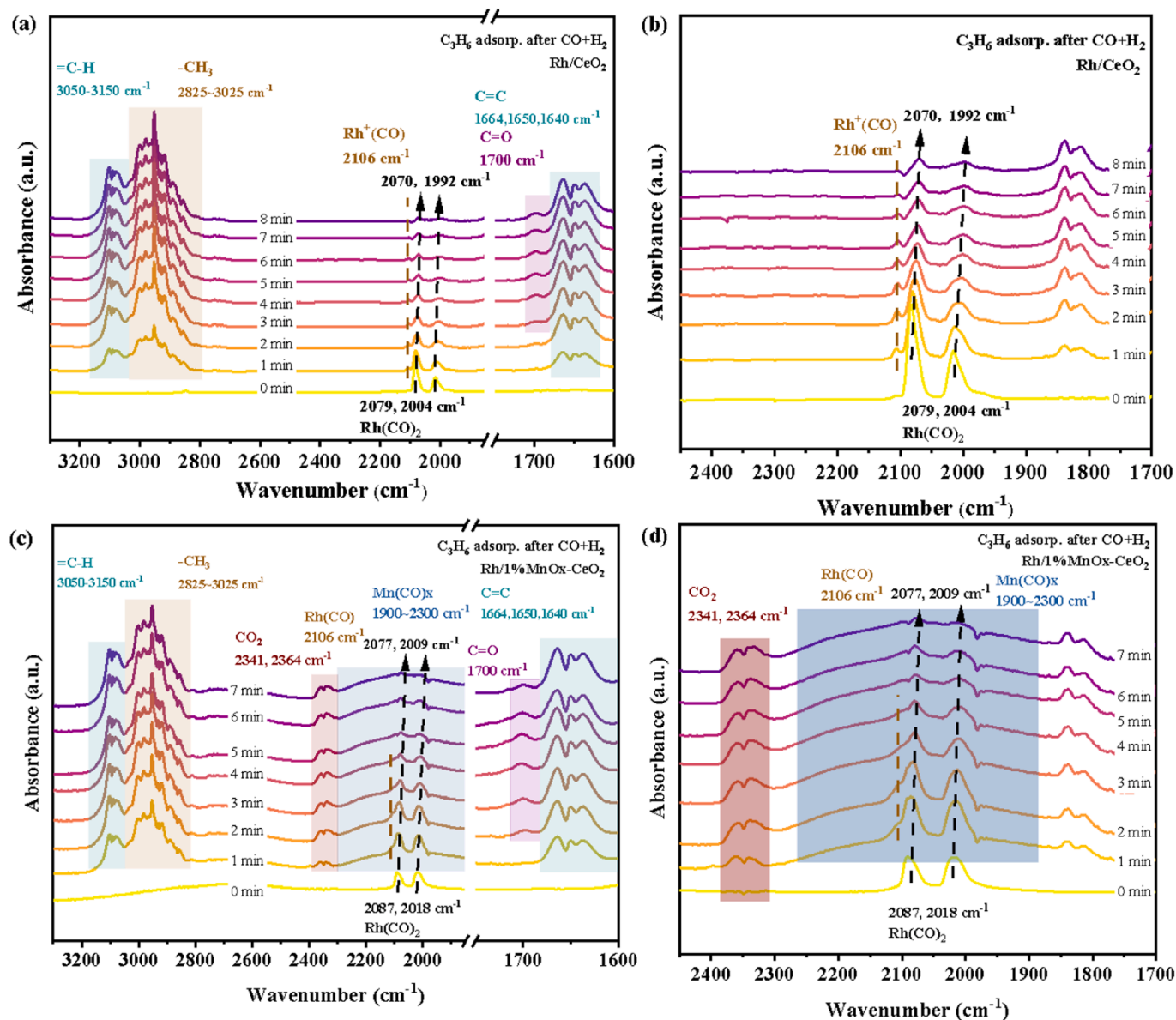


Fig. 6. In-situ FTIR spectra and the corresponding magnified spectra in the range of 2450–1700 cm<sup>-1</sup> (usually CO adsorbed species existed) for (a) and (b) Rh/CeO<sub>2</sub> and (c) and (d) Rh/1% MnOx-CeO<sub>2</sub> which are firstly treated by CO and H<sub>2</sub> at 100 °C for 1 h, then purging with C<sub>3</sub>H<sub>6</sub> and meanwhile recording the FTIR signal.

administration, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2024.123923](https://doi.org/10.1016/j.apcatb.2024.123923).

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